High-temperature Hardness and Wear Resistance of Cobalt-based Tribaloy Alloys

Sydney Nsoesie¹, Rong Liu *2, Kuan Jiang 3, Ming Liang 4

^{1,2} Department of Mechanical and Aerospace Engineering, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6^{3,4} Department of Mechanical Engineering, University of Ottawa, 770 King Edward Avenue.

Ottawa, Ontario, K1N 6N5 Canada

¹snsoesie@connect.carleton.ca; *2Rong.Liu@carleton.ca; 3kjian021@uottawa.ca; 4Ming.Liang@uOttawa.ca

Abstract

This article presents an experimental high-temperature hardness and wear resistance of three cobalt-based Tribaloy alloys. They are two hypereutectic Tribaloy alloys, designated as T-400 and T-400C, and one hypoeutectic Tribaloy alloy, designated as T-401. T-400 is a conventional wear-resistant Tribaloy alloy while T-400C and T-401 newly developed with corrosion/oxidation resistance or/and ductility, respectively. A micro hardness tester equipped with a hot stage is employed to perform hardness measurement on individual phases of the alloys at elevated temperatures. The wear resistance of these alloys is evaluated using a pin-on-disc tribometer equipped with a furnace having temperature capacity of 450°C. The experimental results are integrated and the correlations between microstructure, hardness, wear resistance and temperature for these alloys are discussed.

Keywords

Tribaloy Alloy; Laves Phase; Solid Solution; Hardness; Wear Resistance; Temperature

Introduction

Tribaloy alloys are a series of wear resistant nickel- or cobalt-based alloys, containing a large volume fraction of a hard, intermetallic Laves phase that is distributed in a much softer solid solution matrix (Davis, 2002). It is the presence of the large volume fraction of Laves phase that enables these materials to resist wear under poor or unlubricated conditions. The main alloying elements in Tribaloy alloys include molybdenum (Mo) and chromium (Cr). Silicon (Si) is a minor (~ 3 wt%) constituent of Tribaloy alloys, but molybdenum and silicon are added at levels in excess of their solubility limit in order to induce precipitation of Laves phase. The addition of chromium, which is partitioned about one-third in the Laves phase and two-thirds in the solid solution, imparts corrosion resistance to both phases and thus to the whole material as well

(Cameron et al., 1975). Cobalt and nickel can be alloyed with these elements and tend to form a tough matrix. Depending on the contents of Cr, Mo and Si, the alloys vary in microstructure and mechanical properties significantly. In cobalt-based Tribaloy alloys, the intermetallic Laves phase is characterized as the C-14 (MgZn₂) type whose compositions are approximately CoMoSi or/and Co₃Mo₂Si (Anon, 1975).

Tribaloy alloys are usually hypereutectic, containing the primary Laves phase in a range between 30 ~ 70 vol% (Raghu et al., 1997). The allotropic nature of cobalt can cause a either face-centered cubic (fcc) or hexagonal close-packed (hcp) crystal structure or both can be present in Tribaloy alloys depending on heat treatment. The primary dendrite of the Laves phase is a hexagonal structure (Mason et al., 1989). The Laves phase is so abundant in these alloys that its presence governs all the material properties. Accordingly, the effects of the matrix composition in these alloys are less pronounced than in the case of the cobalt-based carbide-strengthened Stellite alloys, The Laves phase is specifically responsible for outstanding abrasion resistance, but it severely limits the material ductility and impact strength. Typical Tribaloy alloys are T-400 and T-800, which rely on a large percentage of hard intermetallic Laves phase (about 45 vol% in T-400 and 55 vol% in T-800) embedded in a cobalt solid solution for wear resistance (Halstead et al., 1985). T-800 has a larger percentage of Laves phase and a higher chromium content, which results in a harder alloy with better corrosion resistance than T-400 (Cameron et al., 1975). In common with other wear-resistant alloys, Tribaloy alloys are generally hard. T-400 has hardness about HRC 55 and T-800 HRC 60. They have high bearing strength, but exhibit low capacity of plastic deformation and low fracture toughness due to the hard brittle nature of the Laves phase (Halstead et al., 1984).

For certain wear-resistant applications a more oxidation and hot-wear resistant Tribaloy type of alloy is required. Insufficient oxidation resistance leads to welding or casting defects. For high-temperature applications, excessive oxidation may result in sticking of moving parts. Therefore, it is advantageous to have access to a Laves phase alloy with further enhanced oxidation and hot-wear resistance. To this end, a new Tribaloy alloy, designated as T-400C, with these features has been developed in recent years (Yao et al., 2006;Xu et al., 2007; Wooda et al., 2010). Mo level is decreased by 9% and Cr level is increased by 65% in this alloy, compared with T-400. The study of Wooda et al (2010) demonstrated that during the self-mated wear of T-400C in a cylinder at 600°C, stable wear protective oxide films or 'glazes' were formed on the alloy surface. Yao et al. (2006) reported that this new excellent metal-on-metal wear exhibited resistance and also caused less wear damage on the mating nitrided 310SS alloy at 482°C in a Cameron-Plint test. This alloy also showed much better corrosion resistance to 65%HNO3 oxidizing acid at 66°C, to 10%H₂SO₄ reducing acid at 102°C and to 5%HCl reducing acid at 66°C than T-400 (Davis, 2002). In some service conditions, the capacities of plastic flow and fracture toughness are important to Tribaloy alloys, for example, when Tribaloy alloys are used for casting dies, blanking dies, deep drawing dies, Improvement in one attribute is often accomplished at the expense of other desirable material properties. For instance, improving wear resistance of materials often results in reducing toughness, weldability, and corrosion resistance. Therefore it is necessary to consider a reasonable balance between these properties when designing and developing new Tribaloy alloys. A novel Tribaloy alloy, designated as T-401, has been developed with significant increase of Cr content to enhance corrosion resistance but with great reduction of Si content to result in a hypoeutectic microstructure; Mo content is reduced slightly in this alloy, compared to T-400 (Yao et al., 2005;Liu et al., 2005;Liu et al., 2007). With this special chemical composition, unlike conventional Tribaloy alloys, T-401 is a hypoeutectic alloy with the primary phase being dendritic Co solid solution and the Laves phase is in the eutectic. The volume fraction of Laves phase in T-401 (about 30 vol%) is much less than those in T-400 and T-800 due to the significant reduction of Si content thus the change in microstructure. The reduction of Laves phase made this alloy more ductile, which was investigated by Liu

et al. (2005). The corrosion test in the Zn-Al bath at 470°C showed that T-401 exhibited excellent corrosion resistance to molten Zn-Al bath, which was attributed to its hypoeutectic microstructure, higher ductility and less amount of eutectic constituent, as reported by Yao et al. (2005).

This research was aimed to further investigate the properties of the three Tribaloy alloys: T-400, T-400C and T-401, with the emphasis on temperature influence on their hardness and wear resistance. The experimental results were analyzed to explore the correlations between the microstructure, hardness and wear resistance of these alloys and also to investigate the influence of temperature on these properties.

Experimental Details

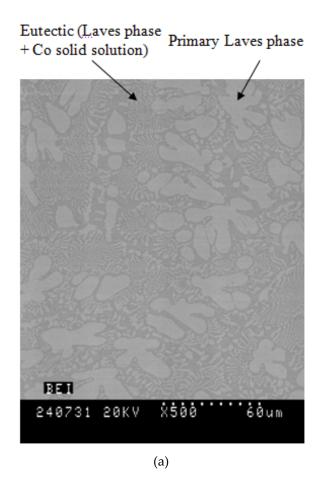
Ribaloy Alloy Specimenst

The chemical compositions of the alloys under study are given in TABLE 1. The specimens were fabricated from a centrifugal casting process, provided by Kennametal Stellite Inc. Each specimen surface was ground with grit papers from course #180 to fine #600 and polished with abrasive cloth plus 1 μ m alumina powders. For microstructural analysis and microhardness test, the polished surface was etched electrolytically using an aluminum cathode at a voltage of 3 V for about 10 s. The etchant is a mixed solution containing 9 g CrO₃, 15 ml HCl and 150 ml H₂O.

The backscatter images of their microstructures, obtained on a Tescan Vega-II XMU Scanning Electron Microscope (SEM) equipped with an Oxford X-ray detection system (INCA EDX) for elemental analysis and quantitative mapping, are shown in FIG. 1. Comparing the three microstructures, T-401 is different largely from T-400 and T-400C in that the primary phase of T-401 is the dendritic Co solid solution while those of T-400 and T-400C are the dendritic Laves phase. T-400C has a similar microstructure to T-400.

TABLE 1 CHEMICAL COMPOSITIONS (WT%) OF TRIBALOY ALLOYS

Element	Со	Cr	Mo	Si
Alloy				
T-400	Bal.	8.5	28.5	2.6
T-400C	Bal.	14	26	2.6
T-401	Bal.	17	22	1.2



Eutectic (Laves phase + Co solid solution)

Primary Laves phase + Co solid solution)

REIL | 809017 20KV X500 60um

(b)

Eutectic (Laves phase Primary Co solid + Co solid solution) solution

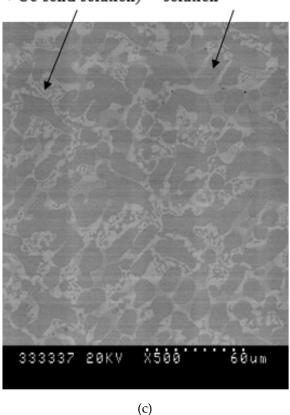


FIG. 1 SEM MICRIOSTRUCTURES O (A) T-400, (B) T- 400C AND (C) T-401

The volume fractions of Laves phase in these alloys were estimated with the associated software of SEM image analysis; the results are given in TABLE 2, together with the Rockwell hardness values of these alloys. It is evident that the hardness of Tribaloy alloys strongly depends on the volume fraction of Laves phase. The larger the volume fraction of Laves phase, the harder the alloy.

TABLE 2 VOLUME FRACTIONS OF LAVES PHASE AND MACRO HARDNESS OF TRIBALOY ALLOYS

	T-400	T-400C	T-401
Volume fraction of Laves phase (vol%)	~ 45	~ 40	~ 30
Rockwell hardness (HRC)	~ 55	~ 53	~ 48

Micro Hardness Test

A Microhardness Tester Unit, Model SMT-X7 Dual Indenter, was utilized to investigate the hardness of the alloys on micro level. To achieve the temperature capacity of 700°C, a Hot-Stage Assembly was attached

to the platform of the tester. This instrument enables indentation to be made on individual phases of a microstructure. The indentation load can vary between 1 to 2000 gf. A low load of 100 gf was selected for this study to insure that the indentation could be made on single phase, because if the load was too high, the indenter would cover an area with other phases involved.

The indentation for each specimen was conducted at room temperature, 250°C and 450°C. The heating and cooling rate was 50°C/min. Five indentation tests were made at each temperature for each specimen and two specimens were tested for each alloy. For each test condition, the average of the results was taken as the final hardness value.

Pin-on-Disc Wear Test

The wear resistance of T-400, T-400C and T-401 was evaluated using a Pin-on-Disc Tribometer at room temperature, 250°C and 450°C. The testing apparatus has a small furnace surrounding the disk and allows the pin going through the top cover to make contact with the specimen surface on a disk in an almost enclosed environment. The apparatus is capable of heating the specimen to a temperature up to 450°C. The pin has a ball shape with a diameter of 5 mm. It is made of 94% WC-6% Co with a hardness of HV 1534. The disk is a circular plate (~5 mm thick) on which the specimen is mounted.

During the test, the disk (specimen) was spinning at a rotational speed of 350 rpm, and the pin (ball) was placed at a distance of 3 mm away from the rotation center on the specimen under a compressive force of 10 N without lubrication. As a result of friction/wear, a circular wear track was created in the specimen surface. The wear loss was evaluated by calculating the volume of the wear track after the specimen surface was worn for 2.5 hr. Three specimens were tested for each alloy at each temperature.

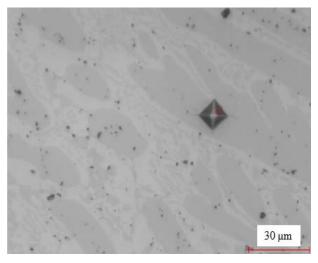
Results and Discussion

Temperature-Dependent Hardness

Tribaloy alloys consist of two phases, Laves phase and solid solution; therefore, the indentation was made on these two phases, separately, for each alloy specimen, as shown in FIG. 2 to FIG. 4. The hardness results are summarized in FIG. 5. Firstly, it is shown that Laves phase is much harder than solid solution for all the

alloys. From the microscopic images, the size of indentation mark in the Laves phase is smaller than that in the solid solutions, which implies that the Laves phase is harder than the solid solutions. Secondly, both Laves phase and solid solution of these alloys behaved differently at room temperature and at elevated temperatures. They were softened by temperature.

Between these two phases, solid solution seems more sensitive to temperature, as the reductions in hardness of Laves phase at 450°C are 4.86%, 6.69% and 26.64% for T-400, T-400C and T-401, respectively, while the reductions in hardness of solid solution at 450°C are 6.26%, 14.33% and 28.44% for these three alloys, respectively. Thirdly, both Laves phase and solid solution of T-401 are much softer than those of T-400 and T-400C. Also, T-400C is softer than T-400 in both phases.



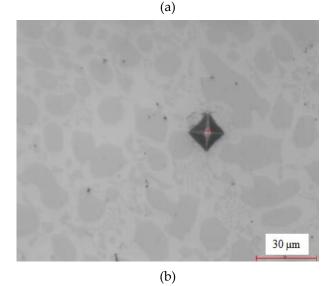
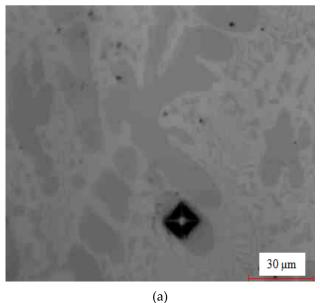


FIG. 2 MICROSCOPIC IMAGES OF INDENTATION MARK IN T-400 SPECIMEN TESTED AT ROOM TEMPERATURE: (a) LAVES PHASE AND (b) SOLID SOLUTION



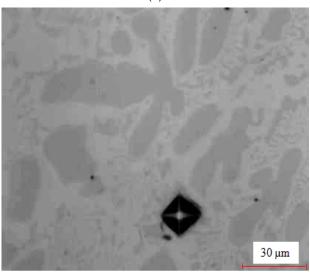
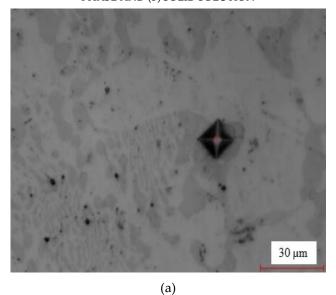


FIG. 3 MICROSCOPIC IMAGES OF INDENTATION MARK IN T-400C SPECIMEN TESTED AT ROOM TEMPERATURE: (a) LAVES PHASE AND (b) SOLID SOLUTION

(b)



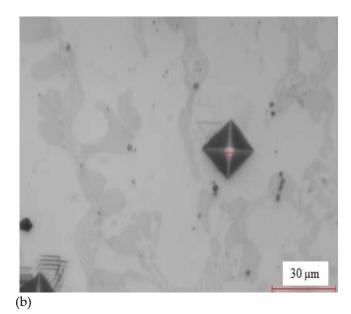
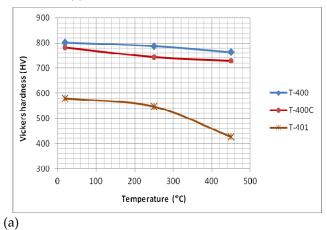


FIG. 4 MICROSCOPIC IMAGES OF INDENTATION MARK IN T-401 SPECIMEN TESTED AT ROOM TEMPERATURE: (a) LAVES PHASE AND (b) SOLID SOLUTION



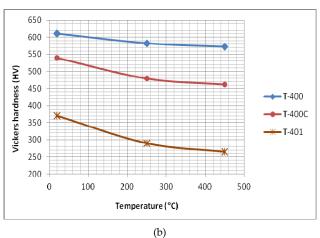
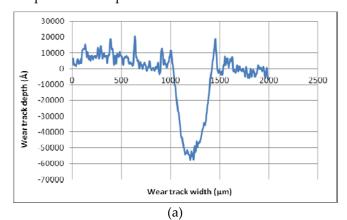


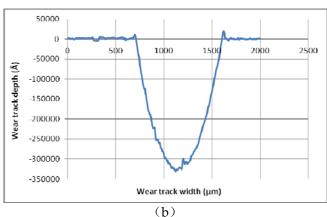
FIG. 5 VICKERS HARDNESS VERSUS TEMPERATURE: (a) LAVES PHASE AND (b) SOLID SOLUTION

Temperature-Dependent Wear Resistance

A D150 Surface Profile Measuring System was employed to measure the cross-sectional profile and thus to calculate the cross section area of the wear track

in each specimen. For each wear track, four different locations were measured and the system software calculated the cross sectional area automatically. Typical cross section profiles of wear tracks for T-400C tested at room temperature and at elevated temperatures are presented in FIG. 6.





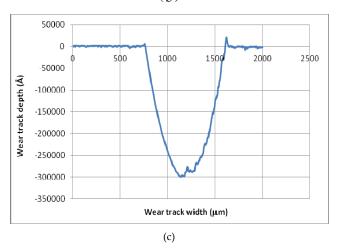


FIG. 6 CROSS SECTION PROFILES OF WEAR TRACK IN T-400C WORN SURFACE TESTED: (a) AT ROOM TEMPERATURE, (b) AT 250°C AND (c) AT 450°C

The average of the four cross-sectional areas was multiplied by the circumferential (circular) length of the wear track to obtain the volume of the wear track, which was deemed to be the material's wear loss. The average wear losses of each alloy at room temperature

and at elevated temperatures are presented in FIG. 7.

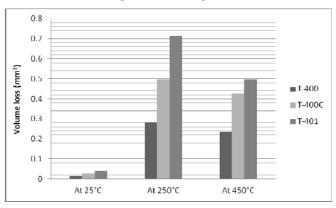


FIG. 7 WEAR LOSS VERSUS TEMPERATURE OF TRIBALOY ALLOYS UNDER PIN-ON-DISC WEAR TEST

It is shown that the wear resistance of Tribaloy alloys varied with temperature; they were more wear resistant at room temperature. At 250°C, the wear resistance of these alloys decreased significantly. However, at 450°C, the wear resistance was improved. Among these alloys, T-400 was the most wear-resistant and T-401 was the least, but the improvement in wear resistance at 450°C was more pronounced on T-401.

Discussion on Hardness Results

Tribaloy alloys are two-phase alloys, consisting of Laves phase and solid solution. The micro indentation test demonstrated that Laves phase was much harder than solid solution for all the alloys being studied, as illustrated in FIG. 5. The Laves phases of these three alloys exhibited different hardness, as seen in FIG. 5(a). Those of the hypereutectic alloys had similar hardness, but that of the hypoeutectic alloy was much softer. It was reported in literature that the Laves phase of T-400 and T-401 was approximately CoMoSi or/and Co₃Mo₂Si (Mason et al., 1989;Xu et al., 2007) and that of T-400C was CoMoSi (Xu et al., 2007). These different forms of Laves phase may have different hardness. Although T-400 and T-401 all have the Laves phase in CoMoSi or/and Co₃Mo₂Si forms, the amounts of these two forms present in the alloys may be different, which can result in the discrepancy of hardness between the two alloys. The solid solution of T-401 is also the softest, followed by T-400C, as seen in FIG. 5(b). This may be due to the less Mo content in T-401, compared with T-400 and T-400C, because element Mo is the main strengthener of solid solution in Tribaloy alloys (Davis, 2002). T-400 contains more Mo than T-400C so that the solid solution of the former is harder than that of the latter. Considering the temperature-dependence of hardness, both the phases of Tribaloy alloys can be softened by temperature, as illustrated in FIG. 5. This may be due to the promoted atomic motion and relief of dislocations or stresses.

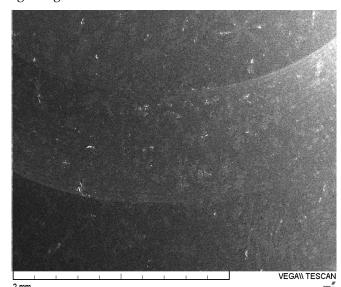
Discussion on Wear Loss Results

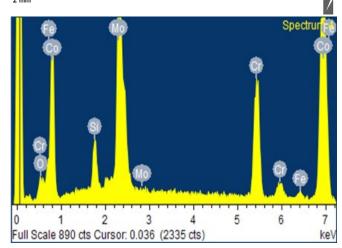
The pin-on-disc sliding wear test showed that T-401 had the lowest resistance among the alloys being studied. This is because this alloy has a hypoeutectic microstructure with Co solid solution as the primary phase thus much less Laves phase present in the microstructure. T-400 had better wear resistance than T-400C at both room temperature and at elevated temperatures. The better wear resistance of T-400 was attributed to the higher hardness of both Laves phase and solid solution as well as the larger volume fraction of Laves phase.

At the elevated temperature of 250°C, the wear resistance of these alloys all decreased significantly, as illustrated in FIG. 7. High-temperature wear of metallic materials involves two main mechanisms, one is softening of the material; the other is oxidation of the material. Due to the high Cr content, these three alloys would be oxidized at high temperatures, forming hard and strong Cr-richoxide films on the specimen surfaces. These oxide films could prevent the surfaces from further oxidation, however, since they were also brittle and vulnerable, under the mechanical attacks in the wear process, the films were inevitably broken, spalled off the specimen surfaces. The oxide debris, on one hand, added to the wear losses of the alloys, on the other hand, it was squeezed into the surface layers of the specimens under the wear loads, which hardened the surfaces, resulting in the increase in wear resistance. This is the so-called "glazing" effect, which commonly occurs on oxidable metals in high-temperature wear.

In order to better understand the wear test results and explore the wear mechanisms of these alloys at room temperature and at elevated temperatures, the worn surfaces of each specimen were analyzed using SEM/EDX. As discussed above, the wear test results showed that at 250°C these alloys exhibited much higher wear loss than at room temperature. Referring to the worn surfaces of these alloys tested at this temperature, they look very smooth and the EDX spectra of the wear tracks show little amount of oxygen present. This implies that at this temperature oxidation was not the main cause for wear loss; instead material softening resulted in reduction of strength, thus decreasing the wear resistance. The worn surfaces together with the EDX spectra for T-400C tested at 250°C and at 450°C are presented in FIG. 8 as an

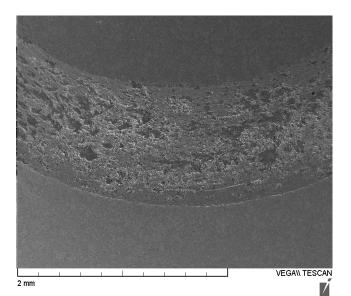
example. Those for T-400 and T-401 have the similar morphologies and characteristics to the worn surface of T-400C. Comparing the worn surface in FIG. 8(a) with that in FIG. 8(b), a large amount of oxide residuals (in white) were observed in the latter, which implied that at the high temperature of 450°C, the specimen surface was seriously oxidized; the EDX spectrum in FIG. 8(b) confirmed this observation with the high oxygen content detected in the wear track. The enhanced wear resistance of these alloys at this temperature should be attributed to the beneficial "glazing" effect.

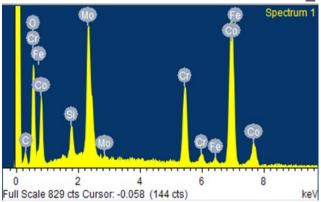




Element	Weight%	Atomic%
Si K	2.92	6.58
Cr K	14.46	17.51
Fe K	1.08	1.22
Co K	51.55	55.02
Mo L	29.99	19.67
Total	100.00	100.00

(a)





Element	Weight%	Atomic%
OK	24.93	56.38
Si K	1.71	2.21
Cr K	11.47	7.98
Fe K	0.84	0.54
Co K	41.78	25.62
Mo L	19.26	7.26
Total	100.00	100.00

FIG. 8 WORN SURFACES WITH EDX SPECTRA OF T-400C TESTED: (a) AT 250°C AND (b) AT 450°C

In addition, as seen in FIG. 7, the wear resistance of T-401 at 450°C was improved more than the others, which implied that the "glazing" effect was more pronounced on this alloy. There are two reasons for this; one is that this alloy contains higher Cr content, which promoted formation of Cr-rich oxides at high temperatures; the other is due to the less volume fraction of Laves phase in this alloy thus larger proportion of tough solid solution matrix present, which provided more surface areas for oxide debris embedded into the specimen, since Laves phase are too

brittle to take in oxide debris.

Conclusions

Two hypereutectic Tribaloy alloys, T-400 and T-400C, and one hypoeutectic Tribaloy alloy, T-401, were studied in hardness and wear resistance at both room temperature and elevated temperatures. The Laves phase and solid solution of T-401 were much softer than those of T-400 and T-400C. T-400 was harder than T-400C in both the phases. The higher hardness of the solid solution was attributed to the higher Mo content, while the difference in hardness of Laves phase was due to the different types of Laves phase and their amounts present in the alloys. The hardness of Laves phase and solid solution of Tribaloy alloys decreased with temperature.

Owing to the higher hardness and larger volume fraction of Laves phase, T-400 exhibited better pin-on-disc sliding wear resistance than T-400C and T-401. The wear resistance of these alloys decreased at elevated temperatures, which was due to the softening of the constituent phases. However, at high temperatures, material oxidation played an important role in affecting the wear loss of these alloys. Because of the high Cr content, a large amount of Cr-rich oxides could be formed on the specimen surfaces at high temperatures. Consequently, the "glazing" effect benefited the wear resistance of these alloys, in particular, it contributed more significantly to that of T-401.

The significant contributions of this research are two: (1) The correlations between chemical composition, microstructure, hardness and wear resistance, derived on T-400, T-400C and T-401, can be a guideline in design of new Tribaloy alloys for different industrial applications. (2) The high-temperature hardness and wear behavior investigated on T-400, T-400C and T-401 can help the material industry use Tribaloy alloys properly.

ACKNOWLEDGEMENT

The authors are grateful for financial support from Natural Science & Engineering Research Council of Canada (NSERC), in-kind support from National Research Council Canada, and both financial and in-kind supports of Kennametal Stellite Inc.

REFERENCES

Anon, "Unique intermetallics combat wear and corrosion." Metal. Prog. 107(5) (1975): 90-92.

- Cameron CB, Hoffman RA and Poskitt RW, "Tribaloy intermetallic alloy compositions new materials or additives for wear resistant applications." Prog. Powd. Metall. 31 (1975): 41-51.
- Cameron CB and Ferriss DP, "Tribaloy intermetallic materials: new wear- and corrosion-resistant alloys." Anti-Corr. Meth. Mater. 22(4) (1975): 5-8.
- Davis JR, Nickel, Cobalt, and Their Alloys, ASM International, Materials Park, 2000, p 362-406.
- Halstead A and Rawlings RD, "Structure and hardness of Co-Mo-Cr-Si wear resistant alloys (Tribaloys)." Metal Sci. 18(10) (1984): 491-500.
- Halstead A and Rawlings RD, "Effect of iron additions on the microstructure and properties of the "Tribaloy" Co-Mo-Cr-Si wear resistant alloys." J. Mater. Sci. 20(5) (1985): 1693-1704.
- Liu R, Yao MX, Patnaik PC and Wu XJ, "Investigation of mechanical behavior of cobalt-based intermetallic materials using a nano-indentation technique." J. Advan. Mater. Special Edition 1(2) (2007): 65-75.
- Liu R, Xu W, Yao MX, Patnaik PC and Wu XJ, "A newly developed Tribaloy alloy with increased ductility."

- Scripta Materialia 53(12) (2005): 1351-1355.
- Mason SE and Rawlings RD, "Structure and hardness of Ni-Mo-Cr-Si wear and corrosion resistant alloys." Mater. Sci. Technol. 5(2) (1989): 180-185.
- Raghu D and Wu JB, "Recent development in wear and corrosion-resistant alloys." Mater. Perform. 36(11) (1997): 27-36.
- Wooda PD, Evansb HE and Pontonb CB, "Investigation into the wear behavior of Tribaloy 400C during rotation as an unlubricated bearing at 600°C." Wear 269(11-12) (2010): 763-769.
- Xu W, Liu R, Patnaik PC, Yao MX and Wu XJ, "Mechanical and tribological properties of newly developed Tribaloy alloys." Mater. Sci. Eng. A 452-453 (2007): 427-436.
- Yao MX, Wu JBC, Xu W and Liu R, "Microstructural characteristics and corrosion resistance in molten Zn-Al bath of Co-Mo-Cr-Si alloys." Mater. Sci. Eng. A 407(1-2) (2005): 299-305.
- Yao MX, Wu JBC, Yick S, Xie YS and Liu R, "High temperature wear and corrosion resistance of a newly developed Laves phase strengthened Co-Mo-Cr-Si alloy." Mater. Sci. Eng. A 435-436 (2006): 78-83.